QUINOXALINE-CONTAINING HYPERBRANCHED AROMATIC POLY(ETHER-KETONES)

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority of the filing date of Provisional Application serial number 60/453,334, filed 02-28-2003.

RIGHTS OF THE GOVERNMENT

The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purposes without the payment of any royalty.

BACKGROUND OF THE INVENTION

The present invention relates to a new quinoxaline-containing hyperbranched ether-ketone polymers.

Dendritic macromolecules such as dendrimers and hyperbranched polymers are a new class of highly branched polymers that have distinctly different properties from their linear analogs. Both dendrimers and hyperbranched polymers have much lower solution and melt viscosities than their linear analogs of similar molecular weights. They also have a large number of chain-ends whose collective influence dictates their overall physical and/or chemical behaviors. These features are attractive in terms of processability and offering flexibility in engineering required properties for specific applications. However, there is a practical advantage that hyperbranched polymers have over dendrimers at "raw material" level. Although dendrimers have precisely controlled structures (designated as generations), their preparations generally involve tedious, multi-step sequences that are impractical and costly in scale-up production. Synthesis of a hyperbranched polymer, on the other hand, is a one-pot process. Large

quantities of hyperbranched polymers can be easily produced from AB_x ($x \geq 2$) monomers.

Because of their excellent thermal and mechanical properties, as well as their optical and electronic characteristics, aromatic, fused heterocyclic polymers such as polyquinoxalines and polybenzoxazoles continue to attract considerable attention. However, they have limited processability due to the nature of fused ring systems. Their insolubility and their softening temperatures are generally above their degradation temperatures. Chemical modification on the these materials, for example, by the use of solubilizing pendants or flexible units in the main chain, has been successful to improve their processability, allowing the optimization of their properties as a function of processability. Another viable approach to achieving this objective is to incorporate the elements of local rigidity and global randomness into the macromolecular architecture. Local rigidity provides the thermal, electronic and optical characteristics of the aromatic fused systems while global randomness frustrates entanglement of the polymer chains, leading to greater solubility. Dendritic structures clearly embody these qualities. However, as noted previously, hyperbranched structures have greater synthetic practicality.

Accordingly, it is an object of the present invention to provide novel quinoxaline-containing hyperbranched poly(ether-ketones).

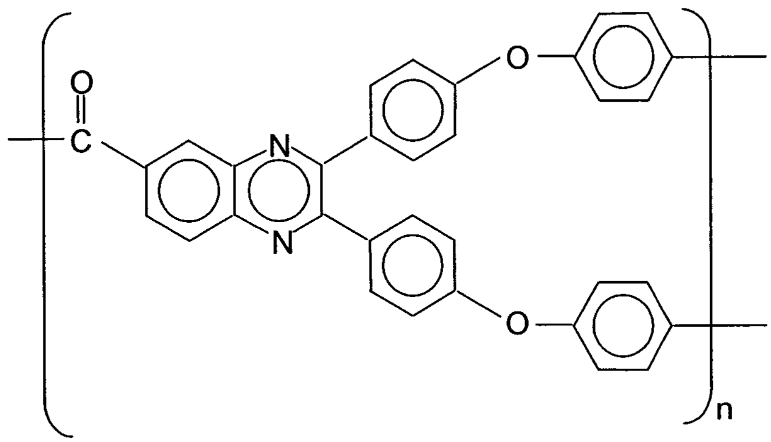
It is another object of the present invention to provide a novel method for preparing quinoxaline-containing hyperbranched poly(ether-ketones).

Other objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be

learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

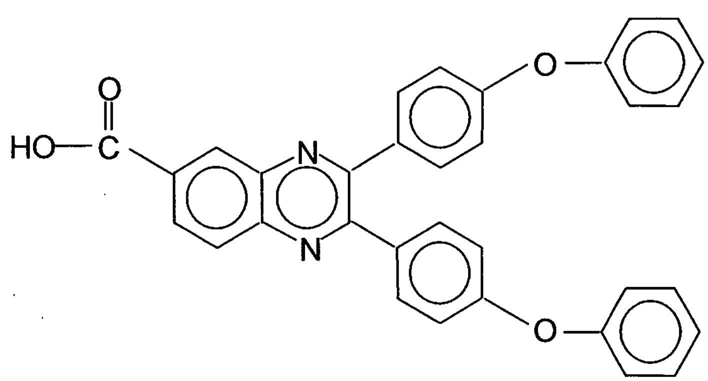
SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a quinoxaline-containing hyperbranched ether-ketone polymer having repeating units of the formula:



DETAILED DESCRIPTION OF THE INVENTION

The quinoxaline-containing hyperbranched ether-ketone polymer of this invention is prepared by polymerization of the corresponding AB_2 monomer



Preparation of the AB_2 monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, is described in co-pending application serial number __________, filed of even date herewith.

Polymerization of the AB_2 monomer can be conducted in polyphosphoric acid (PPA) at a polymer concentration of about 5 weight percent at a temperature of about 130°C. Preliminarily it is helpful to describe the chemistry of phosphoric acids and strong phosphoric acids or polyphosphoric acids as follows: As used herein the term "phosphoric acid(s)" means commercial phosphoric acid(s) containing 85-86% H_3PO_4. The strong phosphoric acids, or polyphosphoric acids referred to as PPA (polyphosphoric acid) are members of a continuous series of amorphous condensed phosphoric acid mixtures given by the formula

$$H_{n+2}P_nO_{3n+1}$$

or

$$HO\text{--}PO_3H_nH$$

where the value of n depends on the molar ratio of water to phosphorus pentoxide present.

In its most general definition, polyphosphoric acid composition can range from distributions where the average value of n is less than unity, giving rise to a mobile liquid, to high values of n, where the polyphosphoric acid is a glass at normal temperatures. Because the species of polyphosphoric acid are in a mobile equilibrium, a given equilibrium composition can be prepared in many ways. For instance, the same distribution or polyphosphoric acid composition could be prepared by either starting with

concentrated orthophosphoric acid (H_3PO_4, n=1) and driving off water or by starting with phosphorus pentoxide (P_2O_5) and adding an appropriate amount of water.

All polyphosphoric acid compositions can be described as a ratio of P_2O_5 and water by reducing the various species present (on paper) to P_2O_5 and water. We will then use the convention that polyphosphoric acid composition will be expressed in terms of a P_2O_5 content (as a percentage) defined as P_2O_5 content

$$= (\text{weight of } P_2O_5) / (\text{weight of } P_2O_5 + \text{weight of water}) \times 100.$$

Thus, the P_2O_5 content of pure orthophosphoric acid could be derived by reducing one mole of H_3PO_4 to 0.5 moles P_2O_5 +1.5 moles H_2O. Converting to weights gives the P_2O_5 content as

$$(0.5 * 142) / ((0.5 * 142) + (1.5 * 18.01)) = 72.4\%$$

Similarly, the P_2O_5 content of commercial polyphosphoric acid can be derived in the following way. Polyphosphoric acid is available commercially in two grades, 105% and 115%. These percentages refer to H_3PO_4 content, which means that 100 g of the two grades contain 105 and 115 grams of H_3PO_4. The P_2O_5 content of 115% polyphosphoric acid can then be calculated knowing the P_2O_5 content of 100% H_3PO_4.

$$(115 * 0.724) / 100 = 83.3\%$$

We have found that the rate of polymerization can be accelerated by adding about 25% additional phosphorus pentoxide (relative to the weight of PPA) to the polymerization mixture, as shown in the examples which follow.

The hyperbranched polymers of this invention are suitable for use in applications where the material will be subject to high service temperatures.

The following examples illustrate the invention:

Example 1

Polymerization of 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline-carboxylic acid (AB_2 monomer) in PPA at 130°C

Into 250 mL resin flask equipped with a high-torque mechanical stirrer and nitrogen inlet and outlet, a pressure regulator, and an addition port, polyphosphoric acid (PPA, 60g) was charged. The PPA was degassed under reduced pressure by freezing in liquid nitrogen and melting in warm water several times. Then the monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline-carboxylic acid (3.0g, 5.9 mmol), was introduced. As soon as the monomer was added and the stirring started, the mixture became deep blue-purple. The mixture was heated to 130°C and kept at this temperature for 48h. Although the mixture had become deep red, its viscosity was not significantly increased. The reaction mixture was allowed to cool to 60-70°C and water was added to precipitate the polymer. The resulting mixture was warm at 60-70°C overnight under the nitrogen. The resulting bright yellow solids were collected by suction filtration, washed with diluted ammonium hydroxide, and large amount of water. The polymer was finally dried under reduced pressure (0.05 mmHg) at 200°C for 150h to give essentially quantitative yield: $[\eta]$=0.07 dL/g (0.5% solution in MSA at 30.0±0.1°C). Anal. Calcd. for $C_{33}H_{20}N_2O_3$ C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 78.69%; H, 4.34%; N, 5.27%; O, 10.81%.

Example 2

Polymerization of AB_2 monomer in PPA/P_2O_5 at 130°C

Into a 250 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, a pressure regulator and an addition port, PPA (83% assay, 80g) was placed and stirred with dried nitrogen purging at 100°C for 10h. The monomer 2,3-

bis(4-phenoxyphenyl)-6-quinoxaline-carboxylic acid (4.0g) was added and heated to 130°C until it become a homogeneous mixture. It usually took about 1 h. The color of mixture became dark brown. P_2O_5 (20.0g ; 25 wt% relative to PPA used) was then added in one portion and the temperature was maintained at 130°C for 24h. The mixture became very viscous after 2h at 130°C and started to stick to the stirring rod. At the end of the reaction, water was added into the flask. The resulting precipitates were collected by suction filtration, washed with diluted ammonium hydroxide followed by a large amounts of water, stirred in boiling water for 100h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 200°C for 48h. The yield was essentially quantitative (>99% yield). Its intrinsic viscosity is 0.56 dL/g (MSA, 30 $\pm$ 0.1°C). Anal. Calcd. for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 80.08%; H, 4.57%; N, 3.69%; O, 10.34%.

Example 3

Polymerization of AB_2 monomer in PPA/P_2O_5 at 160°C

Into a 100 mL resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, a pressure regulator and an addition port, PPA (83% assay, 40g) was placed and stirred with dried nitrogen purging at 100°C for 10h. The monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline-carboxylic acid (1.80g, 3.5 mmol) and P_2O_5 (10.0g) were added and the mixture heated to130°C until it become a homogeneous mixture. It took about 3h. The mixture was then heated at 160°C and it soon stuck to the stirring rod, rendering further efficient stirring/mixing impossible. It took around 3h. At the end of the reaction, water was added into the reaction vessel. The resulting lumps were broken up with the aid of a Waring blender, and the polymer product was

collected by suction filtration, washed with diluted ammonium hydroxide and then with a large amount of water, stirred in boiling water for 100h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 200°C for 48h. The yield was essentially quantitative (>99% yield). The polymer was insoluble in most organic solvents and only formed gel in methanesulfonic acid (MSA). Anal. Calcd. for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%. Found: C, 78.34%; H, 4.34%; N, 5.27%.

Example 4

Polymerization in 1:10 w/w mixture of P_2O_5/Methanesulfonic acid (PPMA) at 110°C

Into a 100 mL 3-necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet, the monomer 2,3-bis(4-phenoxyphenyl)-6-quinoxaline-carboxylic acid (1.0g, 1.96 mmol) and PPMA (10 mL) were added and heated to 110°C for 8h. The color of mixture became dark purple. The mixture was poured into ice water. The resulting purple precipitates were collected by suction filtration, washed with diluted ammonium hydroxide and then with large amount of water, stirred in boiling water for 48h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 200°C for 48h. The yield was essentially quantitative (>99% yield). Its intrinsic viscosity was 0.50 dL/g (MSA, 30 $\pm$ 0.1°C). Anal. Calcd. for $C_{33}H_{19}N_2O_3$: C, 80.47%; H, 4.09%; N, 5.69%; O, 9.75%. Found: C, 78,12%; H, 4.33%; N, 5.27%; O, 10.77%.

The polymerization results are summarized in Table 1.

Table 1. Polymerization Conditions and Yields of Polymer

Example	Media	P_2O_5 (wt%)[a]	Temp. (°C)	Time (h)	[η] dL/g[b]	Yield (%)
1	PPA	0	130	48	0.07	~97
2	PPA	25	130	24	0.56	>99
3	PPA	25	160	3	Gel	>99
4	MSA	10	110	8	0.50	>99

(a) Relative to the amount of PPA used.

(b) Intrinsic viscosity measured in methanesulfonic acid (MSA) at 30±0.1°C.

Thermal Properties. The T_g's of the polymers were determined by DSC. The thermograms were obtained on powder samples after they had been heated to 400°C and cooled to 20°C with heating and cooling rate of 10°C/min. The T_g value was taken as the mid-point of the maximum baseline shift from the second run. The polymer samples (Examples 1-4), which were prepared from different reaction conditions, displayed T_g's at 149°C, 113°C, not detectable, 91°C, in that order. Thermogravimetric analysis of these polymers showed that they were heat-resistant; temperatures at which a 5% weight loss was observed were in the range of 505-525°C in air and 515-536°C in helium, respectively.

Having thus described exemplary embodiments of the present invention, it should be noted by those skilled in the art that the disclosures herein are exemplary only and that alternatives, adaptations and modifications may be made within the scope of the present invention.